

CHAPTER 2

Source Gases: Trends and Budgets

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CHAPTER 2

SOURCE GASES: TRENDS AND BUDGETS

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SCIENTIFIC SUMMARY

Tropospheric growth rates of the major anthropogenic source species for stratospheric chlorine and bromine (chlorofluorocarbons (CFCs), carbon tetrachloride, methyl chloroform, halons) have slowed significantly, in response to substantially reduced emissions required by the Montreal Protocol. Total tropospheric chlorine grew by about 60 pptv (1.6%) in 1992 compared to 110 pptv (2.9%) in 1989. Tropospheric bromine in the form of halons grew by 0.2-0.3 pptv in 1992, compared to 0.6-1.1 pptv in 1989.

Hydrochlorofluorocarbon (HCFC) growth rates are accelerating, as they are being used increasingly as CFC substitutes. Tropospheric chlorine as HCFCs increased in 1992 by about 10 pptv, thus accounting for about 15% of total tropospheric chlorine growth, compared to 5 pptv in 1989 (5% of tropospheric chlorine growth).

The atmospheric residence times of CFC-11 and methyl chloroform are now better known. Model studies simulating atmospheric abundances using more realistic emission amounts have led to best-estimated lifetimes of 50 years for CFC-11 and 5.4 years for methyl chloroform, with uncertainties of about 10%. These models, calibrated against CFC-11 and methyl chloroform, are used to calculate the lifetimes, and hence ODPs (Ozone Depletion Potentials), of other gases destroyed only in the stratosphere (other CFCs and nitrous oxide) and those reacting significantly with tropospheric hydroxyl radicals (HCFCs and hydrofluorocarbons (HFCs)).

Methyl chloride, released from the oceans (natural) and biomass burning (anthropogenic), is a significant source of tropospheric chlorine, contributing about 15% of the total tropospheric chlorine abundance in 1992 (3.8 ppbv). Data collected from the late 1970s to the mid-1980s showed no long-term trend. A paucity of published observational data since means that the likely existence of a global trend in this important species cannot be assessed further.

The total abundance of organic halocarbons in the lower stratosphere is well characterized by *in situ* and remote observations of individual species. Observed totals are consistent with abundances of primary species in the troposphere, suggesting that other source species are not important in the stratosphere. Loss of halocarbons is found as their residence time in the stratosphere increases, consistent with destruction by known photochemical processes. Since the loss of halocarbons produces inorganic chlorine and bromine species associated with ozone loss processes, these observations also constrain the abundance of these organic species in the lower stratosphere.

Volcanoes are an insignificant source of stratospheric chlorine. Satellite and aircraft observations of upper and lower stratospheric hydrochloric acid (HCl) are consistent with stratospheric chlorine being organic, largely anthropogenic, in origin. No significant increase in HCl was found in the stratosphere following the intense eruption of Mt. Pinatubo in 1991. Elevated HCl levels were detected in the eruption cloud of the El Chichón volcano in 1982, but no related change in global stratospheric HCl was observed.

The 1980s were characterized by declining global methane growth rates, being approximately 20 ppbv per year in 1980 declining approximately monotonically to 10 ppbv per year by the end of the decade. Methane growth rates slowed dramatically in 1991-1992, but probably started to increase in late 1993. During 1992 global methane levels grew by only 5 ppbv. The causes of this global anomaly (which manifested predominantly at high latitudes in the Northern Hemisphere) are not known with certainty, but are probably due to changes in methane sources rather than in methane sinks. Global growth rate anomalies have been observed in methane records in the 1920s and 1970s from air trapped in Antarctic ice.

Despite the increased methane levels, the total amount of carbon monoxide (CO) in today's atmosphere is less than it was a decade ago. Recent analyses of global CO data show that tropospheric levels grew from the early 1980s to about 1987 and have declined from the late 1980s to the present. The causes of this behavior have not been identified.

2.1 INTRODUCTION

Recent trends of atmospheric trace gases are important in understanding stratospheric ozone depletion and changes to the current radiative forcing of climate. Estimates of budgets and lifetimes are required to predict future impacts. Likewise, these data are needed to accurately predict what levels of emission reductions are needed in order to stabilize and/or reduce present concentrations. In this assessment we will deal with gases emitted by natural and/or anthropogenic sources that influence the chemical composition of the atmosphere. It includes long-lived gases that contribute to stratospheric ozone depletion (*i.e.*, chlorofluorocarbons (CFCs), halons, nitrous oxide (N₂O)) and/or radiative forcing of the atmosphere (*i.e.*, carbon dioxide (CO₂), CFCs, methane (CH₄), N₂O), and short-lived compounds that are involved in the O₃ chemistry of the troposphere (*i.e.*, carbon monoxide (CO), nitrogen oxides (NO_x), non-methane hydrocarbons). Reduced sulfur gases are important in the formation of tropospheric aerosols and therefore in the climate system; however, these compounds are not included in this Chapter and the reader is referred to Chapter 3 of the IPCC 1994 Interim Report for an updated discussion of these source gases. The current concentrations and recent trends of long-lived gases are summarized in Table 2-1. Lifetimes (*i.e.*, total global burden of the gas divided by its globally integrated sink strength) are also given.

2.2 HALOCARBONS

Halocarbons play an important role in stratospheric ozone depletion and are powerful greenhouse gases. A recent, comprehensive review (Kaye *et al.*, 1994) has provided extensive details on the global distributions, trends, emissions, and lifetimes of CFCs (chlorofluorocarbons), halons, and related species. This section provides an updated summary review.

2.2.1 Tropospheric Distributions and Trends

Tropospheric measurements are mostly made *in situ* at fixed sites distributed between the two hemispheres, supplemented by data collected on ships and aircraft (WMO, 1992). Information on the free tropospheric burdens of atmospheric gases and their time variations has further been obtained through spectro-

scopic remote measurements made from various observational platforms. Recent concentration trends of halocarbons and those reported in the 1991 Assessment (WMO, 1992) are summarized in Table 2-2, indicating that significant changes in trends have been observed for most gases during the last few years. The total Cl increase in 1992 was ~60 pptv/yr, whereas the 1989 increase was ~110 pptv/yr (WMO, 1992).

CFCs AND CARBON TETRACHLORIDE

CCl₃F (CFC-11), CCl₂F₂ (CFC-12), CCl₂FCClF₂ (CFC-113), and carbon tetrachloride (CCl₄) have been measured in a number of global programs and their tropospheric mixing ratios have been increasing steadily over the past fifteen years (Fraser *et al.*, 1994a, and references therein).

There is now clear evidence that the growth rates of the CFCs have slowed significantly in recent years (Figure 2-1), presumably in response to reduced emissions (see Section 2.2.3). CFC-12 and CFC-11 trends in the late 1970s to late 1980s were about 16-20 pptv/yr and 9-11 pptv/yr, respectively. These declined to about 16 and 7 pptv/yr, respectively, around 1990 and to about 11 and 3 pptv/yr by 1993 (Elkins *et al.*, 1993; Khalil and Rasmussen, 1993a; Simmonds *et al.*, 1993; Cunnold *et al.*, 1994; Makide *et al.*, 1994; Rowland *et al.*, 1994).

The global CFC-113 data up to the end of 1990 have been reviewed recently (Fraser *et al.*, 1994a). A global average trend of about 6 pptv/yr was observed for CFC-113, with no sign of a slowing down such as observed for CFCs-11 and -12. However, data up to the end of 1992 now indicate that the growth rate has started to decrease (Fraser *et al.*, 1994a, b, c). Carbon tetrachloride appears to have stopped accumulating in the atmosphere and data collected at Cape Grim, Tasmania, indicate that the background levels of this trace gas may have actually started to decline (Fraser and Derek, 1994).

METHYL CHLOROFORM AND THE HYDROCHLOROFLUOROCARBONS (HCFCs)

Global methyl chloroform (CH₃CCl₃) and HCFC-22 (CHClF₂) data up to the end of 1990 have been reviewed by Fraser *et al.* (1994a), with growth rates in 1990 equal to 4-5 and 6-7 pptv/yr, respectively.

Methyl chloroform data up to the end of 1992 are shown in Figure 2-2, indicating that the slowing of the

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TABLE 2-1. Current atmospheric levels, changes in abundance (1992 minus 1990) and lifetimes of long-lived trace gases. (Adapted from IPCC, 1994a.)

Species	Chem. Formula	mixing ratios (1992) ppbv	growth (1992-1990) ppbv	burden (Tg)	lifetime ^a (years)
CFC-11	CCl ₃ F	0.268	0.005	6.2	50 (±5)
CFC-12	CCl ₂ F ₂	0.503	0.026	10.3	102
CFC-113	CCl ₂ FCClF ₂	0.082	0.005	2.6	85
CFC-114	CClF ₂ CClF ₂	0.020	0.001		300
CCl ₄		0.132	-0.002	3.4	42
CH ₃ CCl ₃		0.160	0.007	3.5	5.4 (±0.4)
CH ₃ Cl		0.600	?	5.0	1.5
HCFC-22	CHClF ₂	0.102	0.014	1.5	13.3
HCFC-141b	CH ₃ CCl ₂ F	0.0003			9.4
HCFC-142b	CH ₃ CClF ₂	0.0035			19.5
CH ₃ Br	(see Chapter 10)				
H-1211	CBrClF ₂	0.0025	0.0001	0.08	20
H-1301	CBrF ₃	0.0020	0.0003	0.05	65
CF ₄		0.070		0.9	50000
C ₂ F ₆		0.004			10000
SF ₆		[0.002-0.003]			3200
N ₂ O (N)		310	1.4	1480	120
CH ₄		1714	14	4850	10 ^b
CO ₂ (C)		356000	2000	760000	(50-200) ^c

^a Lifetimes of additional halocarbons are given in Chapter 13.

^b The adjustment time is 12 to 17 years; this takes into account the indirect effect of methane on its own lifetime (IPCC, 1994a).

^c No single lifetime can be defined because of the different rates of uptake by different sink processes (IPCC, 1994b).

TABLE 2-2. Recent halocarbon trends compared with the values given in the 1991 assessment.

Compound	Period	This Assessment ^a		1991 Assessment ^b	
		pptv/yr	%/yr	pptv/yr	%/yr
CFC-11	90-92	2.5	0.9	9.3-10.1	3.7-3.8
CFC-12	90-92	13	2.6	16.9-18.2	3.7-4.0
CFC-113	90-92	2.5	3.1	5.4- 6.2	9.1
CCl ₄	90-92	-1	-0.8	1- 1.5	1.2
CH ₃ CCl ₃	90-92	3.5	2.2	4.8- 5.1	3.7
HCFC-22	92	7.0	6.9	5- 6	6-7
HCFC-142b	92	~1	~30	n.d.	n.d.
HCFC-141b	93	~0.75	~200	n.d.	n.d.
H-1211	90-92	0.075	3	0.2-0.4	15
H-1301	90-92	0.16	8	0.4-0.7	20
Total Cl		~60		~110	
Total Br ^c		0.2-0.3		0.6-1.1	

^a see text for references

^b 1989 increase (WMO, 1992)

^c bromine in the form of halons

growth rate observed in 1990 has continued, presumably due to reduced emissions in 1991-92 as compared to 1990 and in part to increasing OH levels (1 ± 0.8 %/yr; Prinn *et al.*, 1992). The methyl chloroform calibration problems detailed in Fraser *et al.* (1994a) have yet to be resolved.

Recent global HCFC-22 data (Montzka *et al.*, 1993) indicate a global mixing ratio in 1992 of 102 ± 1 pptv, an interhemispheric difference of 13 ± 1 pptv, and a globally averaged growth rate of 7.3 ± 0.3 %/yr, or 7.4 ± 0.3 pptv/yr, from mid-1987 to 1992. Based on the latest industry estimates of HCFC-22 emissions (Midgley and Fisher, 1993) the data indicate an atmospheric lifetime for HCFC-22 of 13.3 (15.5-12.1) years. Regular vertical column abundances measured by infrared solar absorption spectroscopy in Arizona (32°N), Switzerland (46.6°N) (Zander *et al.*, 1994a), and California (34.4°N) (Irion *et al.*, 1994) have revealed rates of increase of 7.0 ± 0.2 %/yr (1981-1992), 7.0 ± 0.5 %/yr (1981-1992), and 6.5 ± 0.5 %/yr (1985-1990), respectively. Using the

HCFC-22 column abundances obtained at McMurdo, Antarctica (78°S), Irion *et al.* (1994) derived a south-north interhemispheric growth rate ratio of 0.85, in good agreement with the ratio of 0.88 obtained by Montzka *et al.* (1993) from *in situ* surface measurements. The latest 1993 HCFC-22 data indicate that the near-linear trend observed in earlier data has continued (J. Elkins, NOAA; R. Zander, I.A., Univ. of Liege, personal communications to E.S.).

CH₃CClF₂ (HCFC-142b) and CH₃CCl₂F (HCFC-141b) have been recently introduced as CFC substitutes. For HCFC-142b the National Oceanic and Atmospheric Administration (NOAA) flask network results indicate an atmospheric concentration of 3.1 pptv for 1992, with a growth rate of ~ 1 pptv/yr (~ 30 %/yr) (Swanson *et al.*, 1993). The concentration of HCFC-141b for the last quarter of 1992 was 0.36 pptv and 1.12 pptv at the end of 1993 (~ 0.75 pptv/yr or ~ 200 %/yr) (Montzka *et al.*, 1994). Pollock *et al.* (1992) detected upper tropospheric levels of HCFC-142b at about 1.1 pptv in 1989, growing at 7%/yr.

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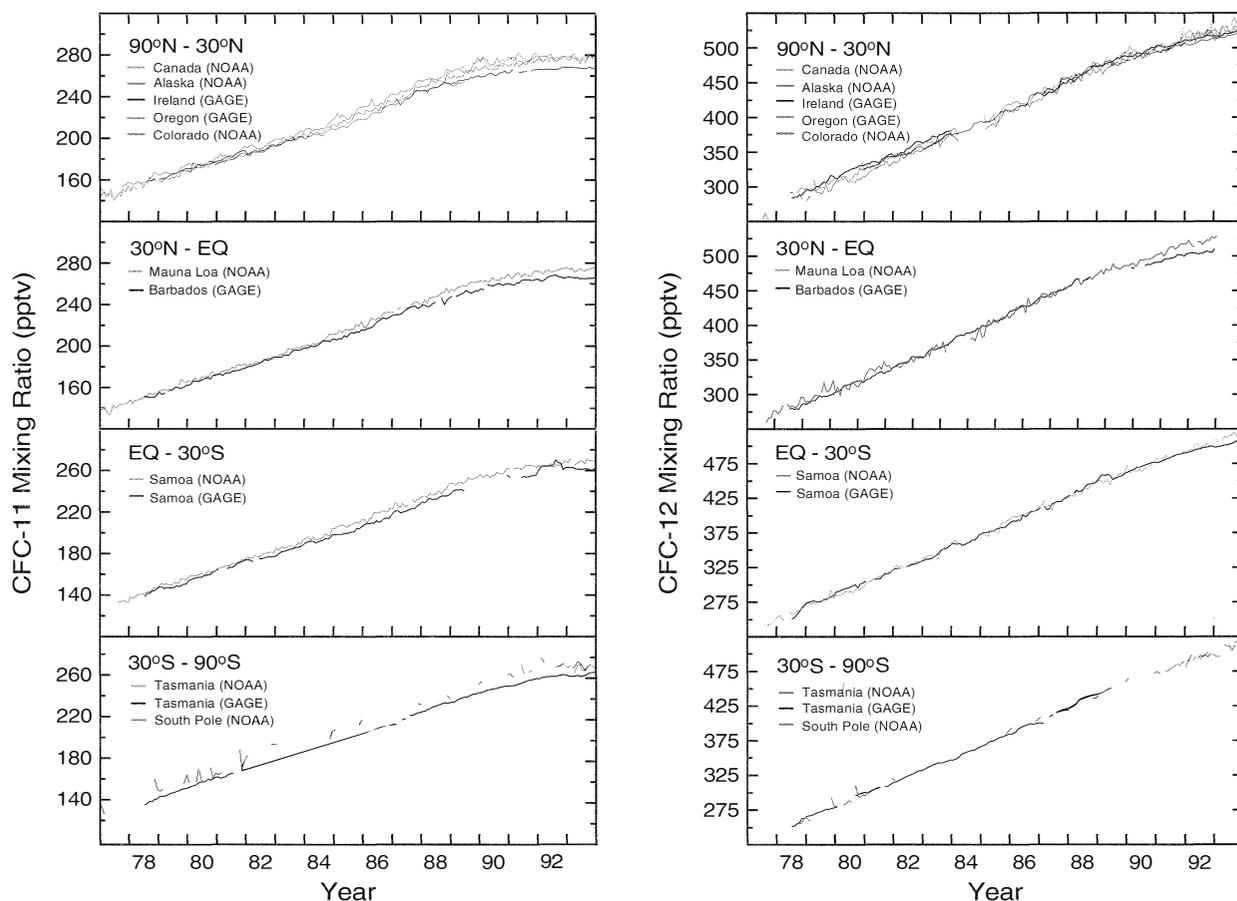


Figure 2-1. a) CFC-11 and b) CFC-12, from the NOAA-CMDL (Elkins *et al.*, 1993) and ALE/GAGE (Cunnold *et al.*, 1994; Fraser and Derek, 1994) global networks. The ALE/GAGE data from 1992 are unpublished and subject to revision.

BROMINATED COMPOUNDS

Recently interest and understanding of brominated species in the background atmosphere have expanded considerably, driven by the recognition of bromine's significant role in stratospheric ozone depletion (*e.g.*, Albritton and Watson, 1992).

The most abundant organobromine species in the lower atmosphere is methyl bromide (CH_3Br), which has both natural and anthropogenic sources. Available data on the global distribution of this gas have been reviewed by Albritton and Watson (1992). An updated evaluation of this important trace gas is given in Chapter 10 of this assessment.

The available halon-1211 (CBrClF_2) and halon-1301 (CBrF_3) data from the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) flask sampling network show that the global background levels are about 2.5 pptv (H-1211) and 2.0 pptv (H-1301), currently growing at about 3%/yr and 8%/yr, respectively (Butler *et al.*, 1992, 1994). These rates have slowed significantly in recent years, consistent with reduced emissions (McCulloch, 1992), and their atmospheric mixing ratios may stabilize in a few years.

Data from the tropical Pacific Ocean (Atlas *et al.*, 1993) indicate concentrations of dibromomethane (CH_2Br_2), bromoform (CHBr_3), and dibromochloromethane (CHBr_2Cl) of 1.8, 1.8, and 0.2 pptv, respectively. Bromoform and dibromochloromethane

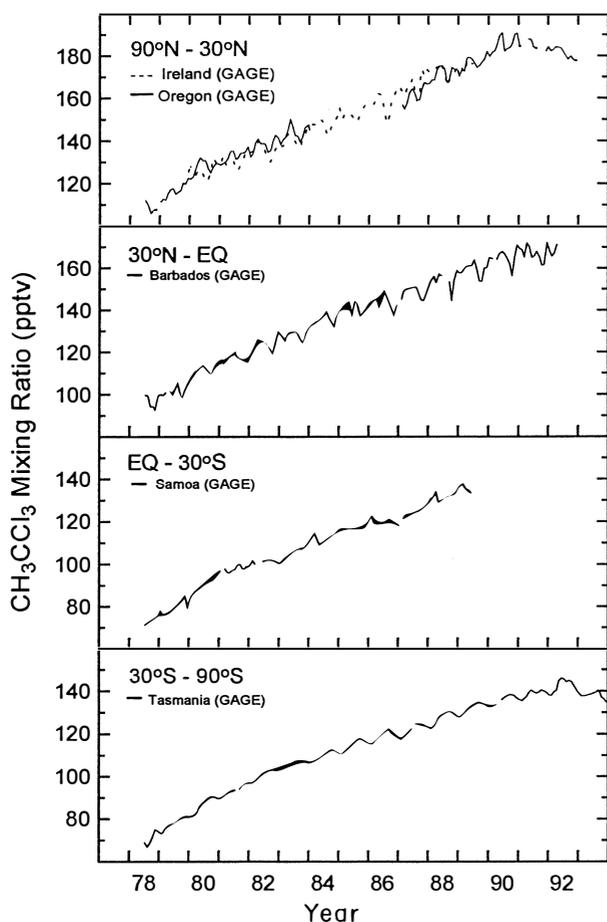


Figure 2-2. Monthly mean methyl chloroform mixing ratios from the ALE/GAGE global network (Prinn *et al.*, 1992; Fraser *et al.*, 1994a; Fraser and Derek, 1994; ALE/GAGE unpublished data).

show distinct equatorial maxima, indicating a tropical source related to natural biogenic activity.

PERFLUORINATED SPECIES

Perfluorinated compounds have very long lifetimes (see Table 2.1) and strong infrared-red absorption characteristics (efficient greenhouse gases). The major loss process appears to be their photolysis in the upper stratosphere and the mesosphere (for details see Chapter 12).

The global mean concentration of carbon tetrafluoride (CF_4) was measured in 1979 at 70 ± 7 pptv (Penkett *et al.*, 1981). This gas has been observed at the South Pole in the late 1970s and mid-1980s at about 65

and 75 pptv, respectively, growing at about 2%/yr (Khalil and Rasmussen, 1985). At northern midlatitudes in the mid-1980s, Fabian *et al.* (1987) reported CF_4 and C_2F_6 concentrations at about 70 pptv and 2 pptv, respectively. There have been no recent reports on CF_4 or C_2F_6 in the background atmosphere.

Sulfur hexafluoride (SF_6) is a long-lived atmospheric trace gas that is about three times more effective as a greenhouse gas than CFC-11 (Ko *et al.*, 1993). Current global background levels are 2-3 pptv, which are apparently increasing with time at about 8.3%/yr (surface measurements; Maiss and Levin, 1994) and $9 \pm 1\%$ /yr (lower stratosphere measurements; Rinsland *et al.*, 1993). IR column measurements in Europe (1986-1990) and North America (1981-1990) indicate increases of $6.9 \pm 1.4\%$ /yr and $6.6 \pm 3.6\%$ /yr, respectively (Zander *et al.*, 1991a).

OTHER HALOGENATED SPECIES

Available data on the abundance of methyl chloride (CH_3Cl), chloroform (CHCl_3), dichloromethane (CH_2Cl_2), and chlorinated ethenes have recently been reviewed (Fraser *et al.*, 1994a). No long-term trends of these species have been observed, although they all exhibit distinct annual cycles (summer minimum, winter maximum). These species are relatively short-lived in the atmosphere (see Table 2-1) and their contribution to ozone depletion and climate forcing is minimal. Methyl chloride is a significant source of tropospheric chlorine. Data collected from the late 1970s to mid-1980s showed no long-term trends (Khalil and Rasmussen, 1985). Recent measurements of various of these gases have been made in the Atlantic (45°N - 30°S) (Koppmann *et al.*, 1993) and in the tropical Pacific Ocean (Atlas *et al.*, 1993). Methyl chloride showed practically no interhemispheric gradient, indicative of a large oceanic or tropical source, whereas chloroform, dichloromethane, tetrachloroethylene, and trichloroethylene showed higher concentrations in the Northern Hemisphere likely due to anthropogenic emissions.

Measurements of methyl iodide and chloroiodomethane in the NW Atlantic Ocean indicate that the latter species may be as important as the former in transferring iodine from the oceans to the atmosphere (Moore and Tokarczyk, 1993b).

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Northern Mid- Latitudes

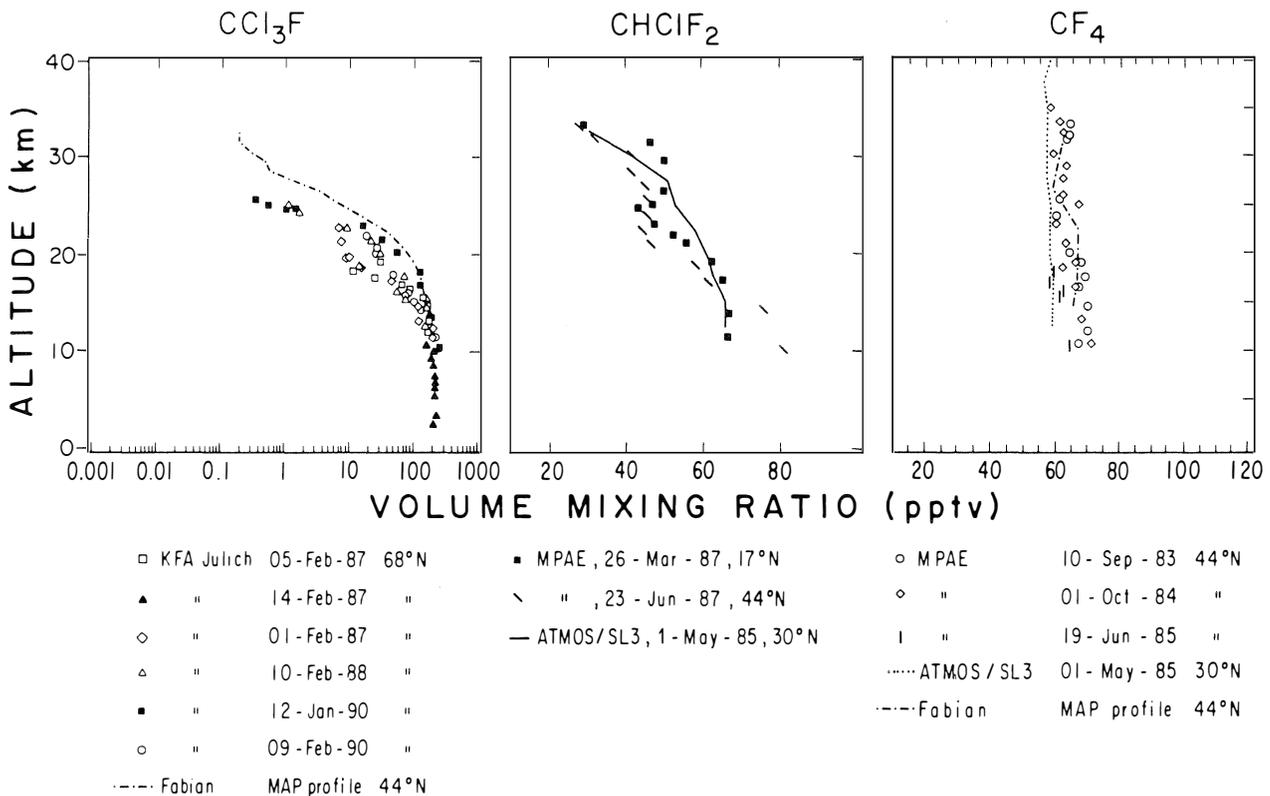


Figure 2-3. Vertical distributions of CCl_3F , CHClF_2 , and CF_4 volume mixing ratios. Source: Adapted from Fraser *et al.*, 1994a.

2.2.2 Stratospheric Observations

When investigating the concentrations of halocarbons in the stratosphere, the main objectives are to determine partitioning among chlorine and bromine “families,” their total loading and their time variations. It is therefore important to measure simultaneously and regularly the largest possible number of halocarbons in order to meet these objectives. For obvious technical reasons, such combined stratospheric measurements have been much sparser during the last decade than tropospheric investigations. The measurements are generally performed using *in situ* air sampling techniques aboard airplane and balloons, and through infrared remote observations made from airplane, balloon, and orbiting platforms.

A recent thorough review dealing with measurements of the stratospheric abundance and distribution of

halocarbons can be found in Chapter 1 of the NASA Report (Fraser *et al.*, 1994a). The review is a compilation of measured concentrations expressed as volume mixing ratios versus altitude for CCl_3F , CCl_2F_2 , CCl_4 , CHClF_2 , CH_3Cl , CH_3CCl_3 , $\text{C}_2\text{Cl}_3\text{F}_3$, $\text{C}_2\text{Cl}_4\text{F}_2$, C_2ClF_5 , C_2F_6 , CClF_3 , CF_4 , CH_3Br , CBrF_3 , and CBrClF_2 , gathered between 1984 and 1990. As an example the concentration profiles for three halogenated methanes at northern mid-latitudes are shown in Figure 2-3. The relative changes in stratospheric concentrations are due to different photochemical destruction rates of these compounds in the stratosphere: $\text{CCl}_3\text{F} > \text{CHClF}_2 \gg \text{CF}_4$.

The *in situ* measurements at sub-tropical, mid- and high northern latitudes of the long-lived chlorinated halocarbons indicate that (i) the concentrations observed in the sub-tropics decline less rapidly with altitude than at midlatitudes, because of increased upward motion at

such latitudes (*i.e.*, Kaye *et al.*, 1991), thus allowing for photodissociation to occur at higher altitudes; (ii) the concentrations of both the halocarbons and the long-lived "reference" gases observed in the Arctic show a much more rapid decline with altitude than at midlatitudes, in particular within the winter vortex where subsidence is often present (Schmidt *et al.*, 1991; Toon *et al.*, 1992a, b, c). Thus, surfaces of constant mixing ratio of long-lived chlorinated halocarbons slope poleward and downward in the lower stratosphere.

During recent years, a few investigations dealing with simultaneous measurements of many chlorine- and/or bromine-bearing gases and related inventories have been reported. One of these concerns the budget of Cl (sources, sinks, and reservoirs) between 12.5 and 55 km altitude, near 30° north latitude, based on the 1985 ATMOS (Atmospheric Trace Molecule Spectroscopy Experiment)/Spacelab 3 measurements of HCl, CH₃Cl, ClONO₂, CCl₄, CCl₂F₂, CCl₃F, and CHClF₂, complemented by results for CH₃CCl₃, C₂Cl₃F₃, ClO, HOCl, and COClF obtained by other techniques (Zander *et al.*, 1992 and references therein). The main conclusions of this work indicate that (i) within the observed uncertainty, partitioning among chlorinated source, sink, and reservoir species is consistent with the conservation of Cl throughout the stratosphere; (ii) the mean 1985 concentration of stratospheric Cl was found equal to 2.55 ± 0.28 ppbv; (iii) above 50 km altitude, the inorganic chlorine burden is predominantly contained in the form of HCl, thus making this measurement a unique and simple way of assessing the effective stratospheric chlorine loading.

Based on historical emissions for the main chlorinated source gases, Weisenstein *et al.* (1992) used a time-dependent model to calculate the atmospheric total chlorine as a function of time, latitude, and altitude. Their results indicate that the total Cl mixing ratio for 1985 reaches an asymptotic value of 2.35 ppbv in the upper stratosphere. Considering that the source input fluxes to the model are probably too low by about 15% because they do not include emission from China, the former Soviet Union, and Eastern Europe, it can be concluded that the result found by Weisenstein *et al.* (1992) for 1985 is in good agreement with the stratospheric Cl budget derived from the 1985 ATMOS observations (Zander *et al.*, 1992).

The ATMOS instrument was flown again in 1992 (Gunson, 1992) and 1993 as part of the Atmospheric Laboratory for Applications and Science (ATLAS) 1 and 2 Missions to Planet Earth. HCl mixing ratios in the range 3.4 ± 0.3 ppbv were measured above 50 km altitude at different latitudes (30°N to 55°S) during March-April 1992, as compared to the measured value of 2.55 ± 0.28 ppbv in April-May 1985 (Gunson *et al.*, 1994). This corresponds to an increase of 35% over the 7 years between both measurements and is in excellent agreement with model-predicted increases of about 0.11 to 0.13 ppbv per year (Prather and Watson, 1990; WMO, 1992; Weisenstein *et al.*, 1992).

During the 1991/92 Airborne Arctic Stratospheric Expedition II (AASE II), a whole air sampler developed by NCAR-NASA/Ames (Heidt *et al.*, 1989) was operated on board the NASA ER-2 aircraft, which attempted to determine the amounts of organic chlorine and bromine entering the stratosphere. Over 600 air samples were collected during AASE II. Twelve of these that were sampled in the latitude/altitude range of the tropical tropopause, between 23.8°N and 25.3°N, have been analyzed by Schauffler *et al.* (1993) for the mixing ratios of 12 chlorinated species (CCl₃F, CCl₂F₂, C₂Cl₃F₃, C₂Cl₂F₄, C₂ClF₅, CHClF₂, CH₃CClF₂, CH₃Cl, CH₂Cl₂, CHCl₃, CH₃CCl₃, and CCl₄) and 5 brominated compounds (CBrF₃, CBrClF₂, C₂Br₂F₄, CH₃Br, and CH₂Br₂). From this extensive suite of measurements, Schauffler *et al.* (1993) derived average total mixing ratios of 3.50 ± 0.06 ppbv for Cl and 21.1 ± 0.8 pptv for Br. The natural source of chlorine is ~0.5 ppbv of the total. Since inorganic chlorine species are negligible at the tropopause, total chlorine at this level is dominated by the anthropogenic release of chlorinated halocarbons at the surface. The stratospheric Cl concentrations derived from the March-April 1992 ATMOS measurements and the January-March 1992 burdens found by Schauffler *et al.* (1993) near the tropopause provide a further confirmation of the conservation of chlorine throughout the stratosphere. The individual contributions to the total organic budget of bromine near the tropical tropopause were found equal to 54% for CH₃Br, ~7% for CH₂Br₂, and the remaining 39% nearly evenly distributed among the halons CBrF₃, CBrClF₂, and C₂Br₂F₄.

On the NASA DC-8 aircraft that also participated in the AASE II campaign, Toon *et al.* (1993) operated a

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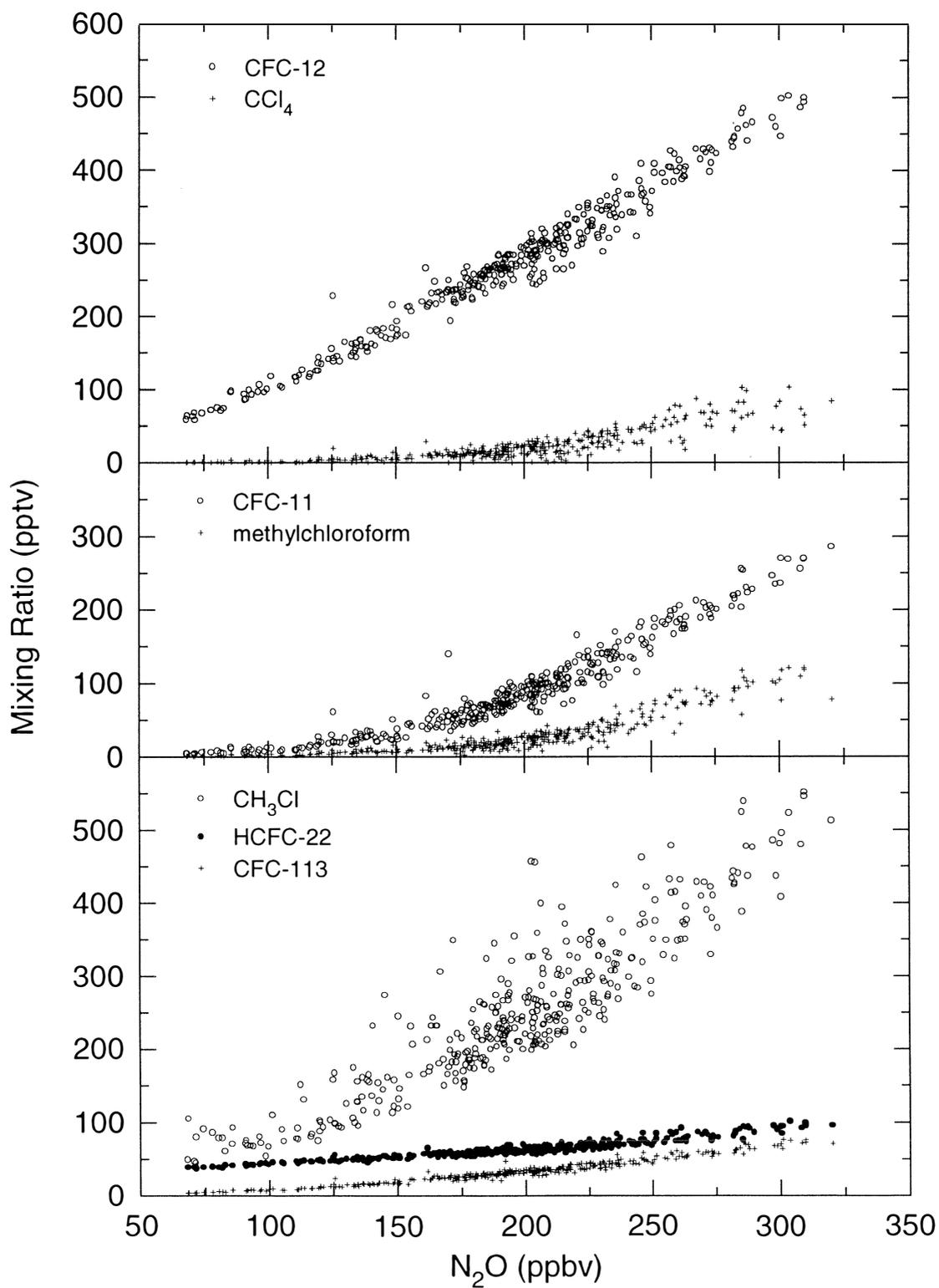


Figure 2-4. Concentrations of halocarbons in the lower stratosphere from NCAR/NASA Ames Whole Air Sampler plotter vs. ATLAS N_2O . Source: Woodbridge *et al.*, 1994.

high-resolution Fourier transform infrared (FTIR) spectrometer to determine the stratospheric columns above about 11 km cruising altitude of a number of trace gases, including CCl_2F_2 and CCl_3F . Based on these and other long-lived gases (*e.g.*, N_2O , CH_4), they found considerably more uplifting (~ 4 km) near the equator than in the sub-tropics.

Above the tropopause, the AASE II data set can be used to describe the depletion of chlorinated halocarbons in the lower stratosphere. As residence time in the stratosphere increases, destruction primarily by UV photolysis liberates Cl and Br from individual halocarbon species, thereby forming the inorganic halocarbon reservoir species HCl and ClONO_2 . Nitrous oxide can be used as an index to examine changes in halocarbon abundances (Kawa *et al.*, 1992). N_2O has a near-uniform abundance in the troposphere of approximately 310 ppbv and is destroyed in the mid-stratosphere with a lifetime near 120 years. Figure 2-4 shows the correlation of several chlorinated halocarbon species with simultaneous measurements of N_2O within the AASE II data set (Woodbridge *et al.*, 1994). The seven species shown represent approximately 99 percent of organic halocarbon species with lifetimes over a year. For each species a distinct correlation is found, with the halocarbon species decreasing with decreasing N_2O . In each case, the decrease begins at upper tropospheric altitudes as reported by Schauffler *et al.* (1993). The slope of each correlation near tropospheric values is related to the ratio of the lifetime of the halocarbons species to that of N_2O (Plumb and Ko, 1992). The compact nature of ranges of these correlations demonstrates the systematic degradation of the chlorinated halocarbons in the stratosphere. The net loss of these organic species over a range of N_2O bounds the available inorganic chlorine reservoir in the lower stratosphere (see Chapter 3). Inorganic species participate in the principal catalytic loss cycles that destroy stratospheric ozone.

The emission of HCl from volcanoes can exceed the annual anthropogenic emissions of total organic chlorine (*e.g.*, CFCs, HCFCs) to the atmosphere. However, emitted HCl is largely removed in the troposphere before it can enter the stratosphere. For the recent Mt. Pinatubo eruption, column measurements of HCl before and after the eruption confirmed that the increase of HCl in the stratosphere was negligible (Wallace and Livingston, 1992; Mankin *et al.*, 1992). Elevated HCl levels

were detected in the eruption cloud of the El Chichón volcano in 1982 (Mankin and Coffey, 1984), but significant changes in the global stratospheric HCl were not observed. The removal of HCl and H_2O is expected to result from scavenging on liquid water droplets formed in the volcanic plume (Tabazadeh and Turco, 1993).

Additional material of relevance to this section can be found in Chapter 3 (Polar Ozone), which also deals with stratospheric abundances of both total organic chlorine and total available chlorine during the Arctic winter; these data may be compared with the mixing ratios of total chlorine quoted here before.

2.2.3 Sources of Halocarbons

CFCs, halons, HCFCs, and hydrofluorocarbons (HFCs) are exclusively of industrial origin, as are methyl chloroform and carbon tetrachloride. Their primary uses are as refrigerants (CFCs-11, 12, and -114; HCFC-22; HFC-134a), foam blowing agents (HCFCs-22 and -142b; CFCs-11 and -12), solvents and feedstocks (CFC-113, carbon tetrachloride, and methyl chloroform), and fire retardants (halons-1211 and -1301). Worldwide emissions of individual halocarbons have fallen significantly following enactment of the Montreal Protocol (Figure 2-5; AFEAS, 1993, 1994; Fisher *et al.*, 1994). From 1988 to 1992 annual emissions of CFCs into the atmosphere have decreased by approximately 34%. Emission levels of methyl chloroform have also declined over this period, with a very large emission reduction ($\sim 50\%$) from 1992 to 1993 (P. Midgley, personal communication to P.F.). HCFC-22 has shown a continued rise (Midgley and Fisher, 1993); it has replaced CFCs in many applications as its use has not been restricted by the Protocol. HCFC-142b release began in the early 1980s and is growing rapidly (35%/yr since 1987). Emissions in 1992 were 10.8×10^6 kg (AFEAS, 1994). Emissions are difficult to estimate accurately as the bulk of the production (90%) is used in closed cell foams with residence times greater than 10 years. Between 1987 and 1990, emissions of halons have dropped substantially (McCulloch, 1992) (no data are available yet for 1991 and 1992). No emission data are available for carbon tetrachloride as its production and use has not been surveyed. A detailed update of the anthropogenic emissions of methyl bromide is given in Chapter 10.

Recently, using the atmospheric data and the equilibrium lifetimes, Cunnold *et al.* (1994) estimated the

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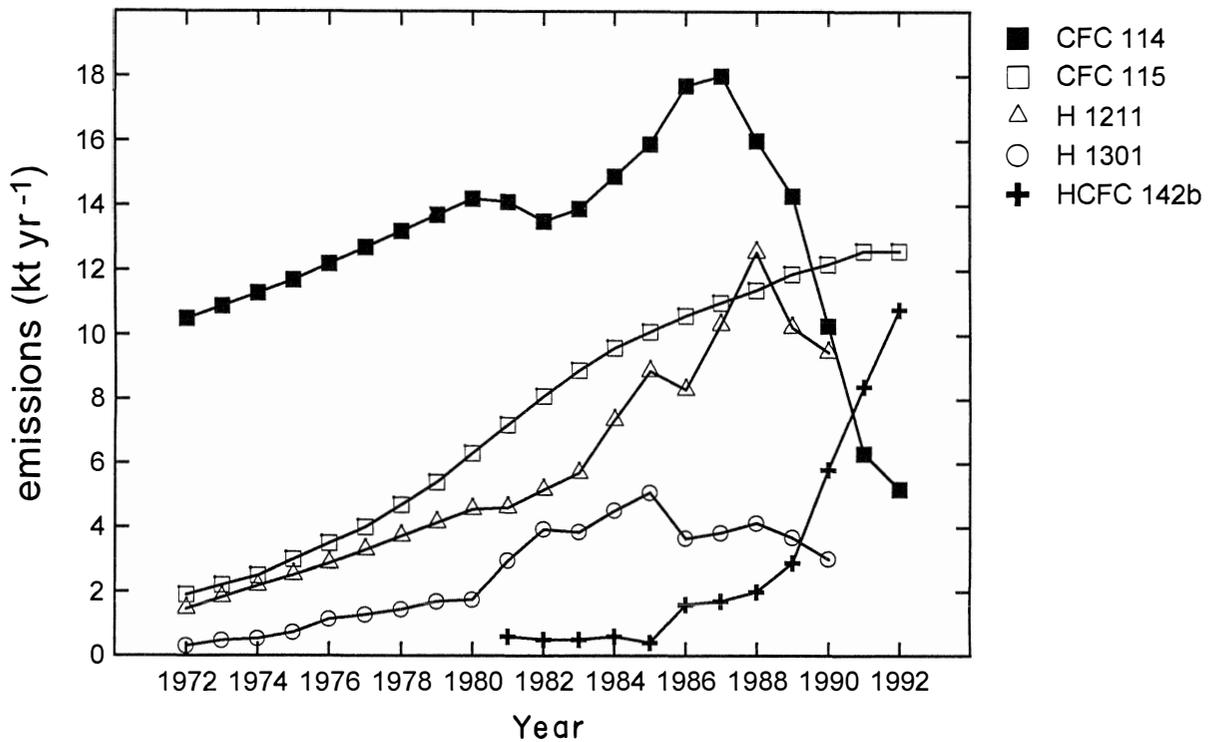
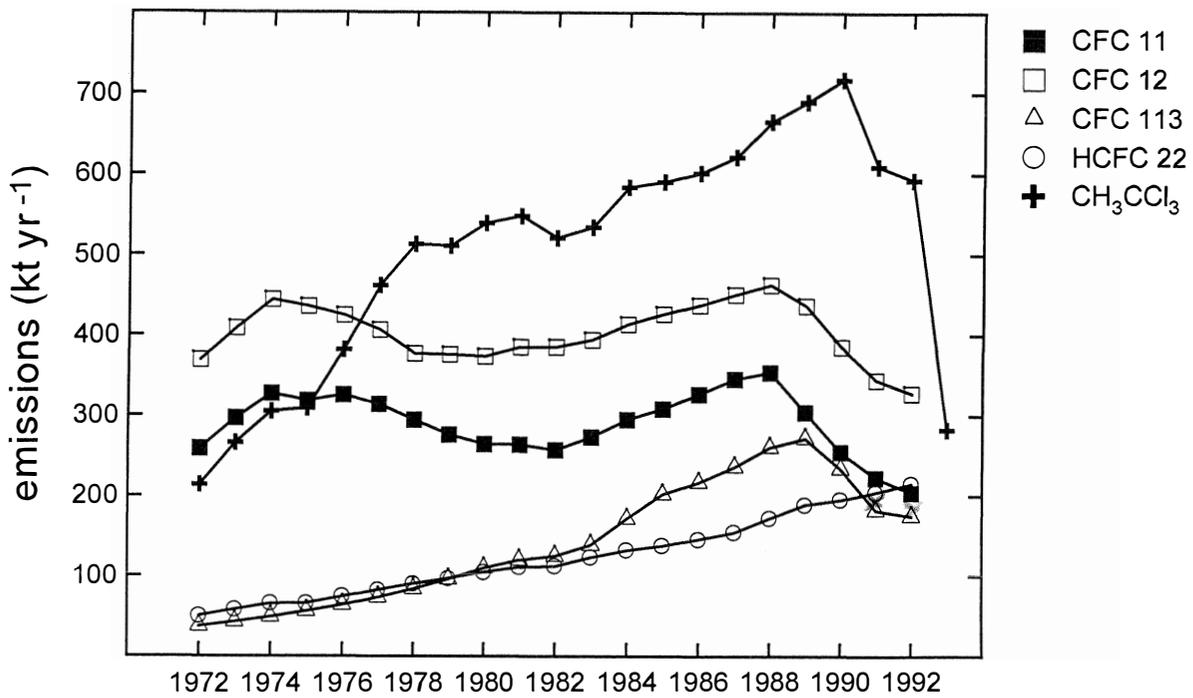


Figure 2-5. Annual emissions of halocarbons in kt/yr. The CFC-11, -12 and -113 data are estimates of global emissions, whereas the remaining estimates are based on data only from reporting companies. Source: AFEAS, 1993; Fisher *et al.*, 1994; D. Fisher, Du Pont, personal communication to P.F.; P. Midgley, M&D Consulting, personal communication to P.F.

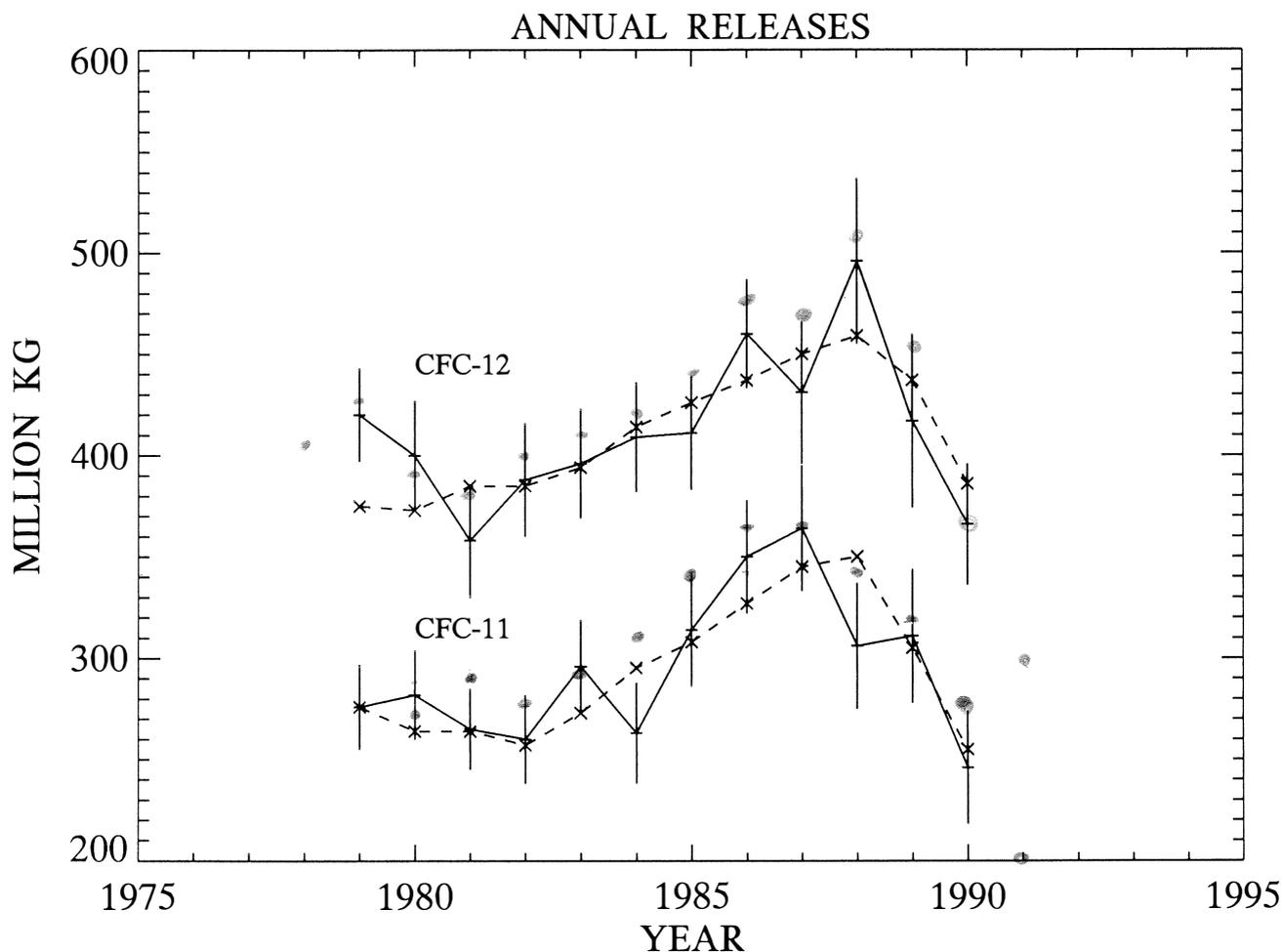


Figure 2-6. Annual releases of CCl_3F and CCl_2F_2 estimated from 13 years of ALE/GAGE data (points are joined by a full line), and most recent estimates of world releases of these compounds (Fisher *et al.*, 1994). Source: Cunnold *et al.*, 1994.

1990 CFC-11 and CFC-12 releases to be 249 ± 28 kton and 366 ± 30 kton, respectively. These values are comparable to the global emissions assembled by Fisher *et al.* (1994) (CFC-11: 255.2 kton and CFC-12: 385.6 kton) (Figure 2-6).

CH_2Cl_2 and CHClCCl_2 are used as industrial cleaning solvents. Sources of 0.9 and 0.6 Tg/yr have been recently estimated from observed atmospheric abundances (Koppmann *et al.*, 1993). Industry estimates of 1992 emissions for CCl_2CCl_2 , CHClCCl_2 , and CH_2Cl_2 were 0.24, 0.16, and 0.39 Tg, respectively. Total emissions for these species have declined by 40% since 1982 (P. Midgley, personal communication to P.F.). The aluminum refining industry produces CF_4 (0.018 Tg/yr)

and C_2F_6 (0.001 Tg/yr), however, there are no estimates of other potential sources (Cicerone, 1979). 80% of SF_6 production (0.005 Tg in 1989) is used for insulation of electrical equipment, 5-10% for degassing molted reactive metals, and a small amount as an atmospheric tracer (Ko *et al.*, 1993). The rate of increase of SF_6 in the atmosphere (Zander *et al.*, 1991a; Rinsland *et al.*, 1993; Maiss and Levin, 1994) implies that its sources are increasing.

Methyl halides are produced during biomass burning. Annual emissions of 1.5-1.8 Tg/yr (Lobert *et al.*, 1991; Andreae, 1993) and 30 Gg/yr (Manö and Andreae, 1994) have been estimated for CH_3Cl and CH_3Br , respectively.

SOURCE GASES

A major source of methyl halides appears to be the marine/aquatic environment, likely associated with algal growth (Sturges *et al.*, 1993; Moore and Tokarczyk, 1993a). Methyl chloride, present in the troposphere at about 600 pptv, is the most prevalent halogenated methane in the atmosphere. Maintaining this steady-state mixing ratio with an atmospheric lifetime of the order of two years requires a production of around 3.5 Tg/yr, most of which comes from the ocean and biomass burning. The atmospheric budget of methyl bromide is discussed in Chapter 10. Other halogenated methanes, such as CHBr_3 , CHBr_2Cl , and CH_2CBr_2 , are produced by macrophytic algae (seaweeds) in coastal regions (Manley *et al.*, 1992) and possibly by open ocean phytoplankton (Tokarczyk and Moore, 1994), but they do not accumulate significantly in the atmosphere.

2.2.4 Halocarbon Sinks

Fully halogenated halocarbons are destroyed primarily by photodissociation in the mid-to-upper stratosphere. These gases have atmospheric lifetimes of decades to centuries (Table 2-1).

Halocarbons containing at least one hydrogen atom, such as HCFC-22, chloroform, methyl chloroform, the methyl halides, and other HCFCs and HFCs are removed from the troposphere mainly by reaction with OH. The atmospheric lifetimes of these gases range from years to decades, except for iodinated compounds such as methyl iodide, which have lifetimes of the order of days to months. However, some of these gases also react with seawater. About 5-10% of the methyl chloroform in the atmosphere is lost to the oceans, presumably by hydrolysis (Butler *et al.*, 1991). About 2% of atmospheric HCFC-22 is apparently destroyed in the ocean, mainly in tropical surface waters (Lobert *et al.*, 1993). Methyl bromide sinks are discussed in Chapter 10.

Recent studies show that carbon tetrachloride may be destroyed in the ocean. Widespread, negative saturation anomalies (-6 to -8%) of carbon tetrachloride, consistent with a subsurface sink (Lobert *et al.*, 1993), have been reported in both the Pacific and Atlantic oceans (Butler *et al.*, 1993; Wallace *et al.*, 1994). Published hydrolysis rates for carbon tetrachloride are not sufficient to support these observed saturation anomalies (Jeffers *et al.*, 1989) which, nevertheless, indicate that about 20% of the carbon tetrachloride in the atmosphere is lost in the oceans.

Recent investigation of the atmospheric lifetimes of perfluorinated species CF_4 , CF_3CF_3 , and SF_6 indicates lifetimes of >50,000, >10,000, and 3200 years (Ravishankara *et al.*, 1993). Loss processes considered include photolysis, reaction with $\text{O}(^1\text{D})$, combustion, reaction with halons, and removal by lightning.

2.2.5 Lifetimes

Lifetimes are given in Table 2-1. An assessment and re-evaluation of the empirical models used to derive the atmospheric residence lifetime of two major industrial halocarbons, CH_3CCl_3 and CFC-11, have been made recently (Bloomfield, 1994). The analysis uses four components: observed concentrations, history of emissions, a predictive atmospheric model, and an estimation procedure for describing an optimal model. An optimal fit to the observed concentrations at the five Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) surface sites over the period 1978-1990 was done with two statistical/atmospheric models: the ALE/GAGE 12-box atmospheric model with optimal inversion (Prinn *et al.*, 1992) and the North Carolina State University/University of California-Irvine 3D-Goddard Institute for Space Studies (NCSU/UCI 3D-GISS) model with autoregression statistics (Bloomfield, 1994). There are well-defined differences in these atmospheric models, which contribute to the uncertainty of derived lifetimes.

The lifetime deduced for CH_3CCl_3 is 5.4 years with an uncertainty range of ± 0.4 yr (IPCC, 1994a). From this total atmospheric lifetime, the losses to the ocean and the stratosphere are used to derive a tropospheric lifetime for reaction with OH radicals of 6.6 yr ($\pm 25\%$); this value is used to scale the lifetimes of HCFCs and HFCs (*e.g.*, Prather and Spivakousky, 1990). On the other hand, the semi-empirical lifetime for CFC-11 of 50 ± 5 years (IPCC, 1994a) provides an important transfer standard for species that are mainly removed in the stratosphere, *i.e.*, the relative modeled lifetimes given in Table 2-1 for CFCs, H-1301, and N_2O are scaled to a CFC-11 lifetime of 50 yr.

A more recent analysis of the ALE/GAGE data (1978-1991) using the ALE/GAGE model and a revised CFC-11 calibration scale (SIO 93) gives an equilibrium lifetime for CFC-11 of 44 (+17/-10) years (Cunnold *et al.*, 1994).

2.3 STRATOSPHERIC INPUTS OF CHLORINE AND PARTICULATES FROM ROCKETS

Solid-fuel rocket motors of launch vehicles release chemicals in the stratosphere, including chlorine (mainly HCl), nitrogen, and hydrogen compounds that, directly or indirectly, can contribute to the catalytic destruction of ozone. Chapter 10 of the WMO-Report No. 25 covers this subject (Harwood *et al.*, 1992). Since that report, which summarized model studies that evaluated the chlorine buildup in the stratosphere and its impact on the ozone layer, based on the projected launches of the larger rocket types (Space Shuttle and Titan IV by Prather *et al.*, 1990, and by Karol *et al.*, 1991; Ariane 5 by Pyle and Jones, 1991), no additional studies have been released. The main conclusions arrived at by Harwood *et al.* (1992) were: i) within the expanding exhaust trail of a large rocket, stratospheric ozone can be reduced substantially, up to >80% at some heights and up to 3 hours after launch; ii) because of the slant layout of the trajectory, column ozone is probably reduced by less than 10% over an area of a few hundred square kilometers; iii) the local plume ozone reductions decrease to near zero within 24 hours and the regional effects are too small to be detected by satellite observations; iv) steady-state model calculations for realistic launch scenarios of large rockets by NASA and ESA (European Space Agency) show that for both scenarios, ozone decreases are less than 0.2% locally in the region of maximum chlorine increase, with corresponding changes in ozone column of much less than 0.1%.

2.3.1 Stratospheric Chlorine Input

The specific chlorine (Cl) input to the stratosphere (above 15 km altitude) from rocket exhausts can be estimated if the Cl amount and its time-dependent release along the ascent are known. Such evaluations were reported by Prather *et al.* (1990) regarding the Space Shuttle (68 tons Cl) and the Titan IV launcher (32 tons Cl), and by Pyle and Jones (1991) for Ariane 5 (57 tons Cl). Assuming a projection of 10 launches per year for each of these chlorine-releasing rocket types, a total of 1570 tons of Cl is then deposited in the stratosphere each year. This corresponds to only 0.064% of the present-day stratospheric burden of chlorine (based on a Cl volume mixing ratio of 3.5 ppbv, or a total of 2.45×10^6 tons of Cl above 15 km altitude). However, at the rate of

increase of the stratospheric chlorine loading measured between 1985 and 1992, *i.e.*, 0.13 ppbv per year (see Section 2.2.2) caused by the release of 30×10^4 tons/yr of Cl from the photodissociation of CFCs in the stratosphere (Prather *et al.*, 1990), the scenario of large rocket launches envisaged here corresponds to an additional injection of Cl above 15 km equal to about 0.6% per year. This percentage will increase as CFCs are phased out. No similar Cl input to the stratosphere can be evaluated for a large number of smaller rockets, because their exhaust characteristics as well as their number of launches worldwide (maybe some 100, all types combined; Harwood *et al.*, 1992) are poorly documented or inaccessible.

2.3.2 Particulates from Solid-Fuel Rockets

Besides gases, solid-fuel rocket motors release particulates in the form of aluminum oxide (Al₂O₃), soot, and ice. Attempts to determine the distribution of exhausted aluminum oxide particles in the rocket exhausts are limited, with only one Shuttle-related set of measurements made some 10 years ago (Cofer *et al.*, 1985) indicating a distribution of particles with significantly more particles below 1 μm than above 1 μm in size. The lack of satisfactory information on rocket particulate releases significantly hampers the quantification of impacts that heterogeneous chemistry (Hofmann and Solomon, 1989; Granier and Brasseur, 1992) may have on ozone depletion by rockets.

The only research programs that have provided some indication about the recent evolution of particulates and aerosols in the stratosphere are by Zolensky *et al.* (1989) and by Hofmann (1990, 1991). From impaction collections sampled in 1978 and 1984, Zolensky *et al.* (1989) found an order of magnitude increase in aluminum-rich particles of >0.5 μm diameter at 17-19 km altitude; they suggested that this rise is likely due to the influx of solid rocket motor exhaust and ablating rocket and satellite debris into the stratosphere in increasingly larger amounts, with the latter predominating. Hofmann (1990) observed an increase by about 80% of the background (non-volcanic) stratospheric sulfate burden at northern midlatitudes between 1979 and 1990. He speculated (Hofmann, 1991) that it may be partially caused by the increase in air traffic during that same period, basing his evaluation on a representative fleet and engine

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emission index of sulfur dioxide (SO₂), as well as on a realistic lifetime for the stratospheric aerosol. However, Bekki and Pyle (1992) concluded that the increase in aerosol mass between 1979 and 1990 due to the rise of air traffic is largely insufficient to account for the observed mass trend and suggest that a rise in submicrometer particles due to the influx of solid rocket exhaust and ablating spacecraft material merits further investigations. Clearly, particulates from solid-fuel rockets deserve careful attention, especially as their stratospheric abundance may increase in the near future.

2.4 METHANE (CH₄)

Methane is an important greenhouse gas that is also a reactive gas that participates in establishing the oxidizing capacity of the troposphere, and therefore affects the lifetime of many other trace gases. In the stratosphere it is a source of hydrogen and water vapor, and a sink of atomic chlorine. It is mainly produced from a wide variety of anaerobic processes and removed by the hydroxyl radical. Its abundance in the atmosphere has been rising since the Industrial Revolution with its global 1992 tropospheric mixing ratio being equal to 1.714 ppmv. A large fraction of methane is released to the atmosphere from anthropogenic sources (~2/3) and is therefore susceptible to possible emission controls. A reduction of about 10% of anthropogenic emissions would stabilize the concentration at today's level (IPCC, 1994a).

2.4.1 Atmospheric Distribution and Trends

Due to the distribution of CH₄ sources, there is an excess Northern Hemispheric source of about 280 Tg/yr, and atmospheric concentrations in the Southern Hemisphere are ~6% lower. Recent modeling (Law and Pyle, 1993) and isotopic (Lasey *et al.*, 1993) studies confirm that the seasonal cycle of methane ($\pm 1.2\%$ at midlatitudes) in the Southern Hemisphere is mainly controlled by the seasonality of methane oxidation by OH radicals in the lower troposphere and the transport of air from tropical regions that are affected by biomass burning.

During the past decade, global methane has increased on average by about 7% (Dlugokencky *et al.*, 1994a). The declining atmospheric methane growth identified in the previous assessment has continued.

Measurements from two global observing networks show a steady decline in the globally averaged growth rate since the early 1980s (Steele *et al.*, 1992; Khalil and Rasmussen, 1993b; Khalil *et al.*, 1993a; Dlugokencky *et al.*, 1994c), being approximately 20 ppbv/yr in 1979-1980, 13 ppbv/yr in 1983, 10 ppbv/yr in 1990, and about 5 ppbv/yr in 1992 (Dlugokencky *et al.*, 1994c). The decline of the growth rate in the 30°-90°N semi-hemisphere was 2-3 times more rapid than in the other semi-hemisphere. The 1992 increase in the Northern Hemisphere was only 1.8 ± 1.6 ppbv (Dlugokencky *et al.*, 1994c). The cause of this global decline in methane growth is not entirely clear, but could be related to changes in emissions from fossil fuel (particularly natural gas) in the former Soviet Union (Dlugokencky *et al.*, 1994c) and from biomass burning in the tropics (Lowe *et al.*, 1994). Observed methane levels in the high Arctic (Alert, 83°N) in 1993 were actually lower than those observed in 1992 (Worthy *et al.*, 1994). Data reported for Antarctica (Aoki *et al.*, 1992) show the same trend observed by the NOAA-CMDL station in the same region. Vertical column abundance measurements above the Jungfraujoch station, Switzerland, between February 1985 and May 1994 indicate a rate of increase in the atmospheric burden of CH₄ equal to 0.73 ± 0.13 %/yr over the period 1985-1989, which slowed to 0.46 ± 0.11 %/yr between 1990 and May 1994 (Zander *et al.*, 1994c; R. Zander, personal communication to E.S.).

A significant decrease in ¹³CH₄ has been observed in the Southern Hemisphere since mid-1991, coincident with significant changes in the CH₄ growth rate (15 ppb/yr in 1991; 5 ppb/yr in 1992) (Lowe *et al.*, 1994). The isotopic data imply that the change in CH₄ growth rate is due to: i) decreasing sources rather than increasing sinks, and ii) a combination of decreased tropical biomass burning and a lower release of fossil CH₄ in the Northern Hemisphere.

Global measurements of CH₄ between 100 and 0.1 mb pressure levels have been performed by various instruments aboard the Upper Atmosphere Research Satellite (UARS). Since October 1991, the UARS Halogen Occultation Experiment (HALOE) has made routine measurements of methane concentrations at latitudes ranging from ~80°N to ~80°S. These measurements have been used in conjunction with other HALOE observations to evaluate vertical subsidence in the Antarctic spring polar vortex (Russell *et al.*, 1993); they have un-

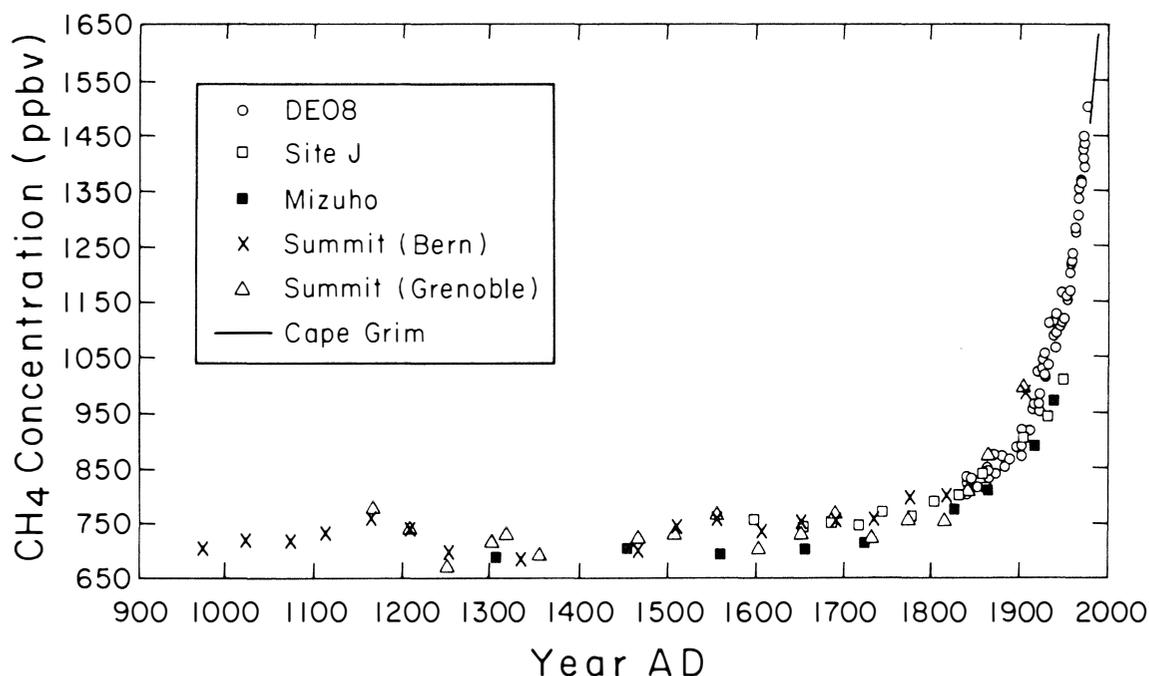


Figure 2-7. Methane mixing ratios observed in ice cores from Antarctica (Law Dome: Etheridge *et al.*, 1992; Mizuho: Nakazawa *et al.*, 1993) and Greenland (Site J: Nakazawa *et al.*, 1993; Summit: Blunier *et al.*, 1993) over the past 1000 years. Atmospheric data from Cape Grim, Tasmania, are included to demonstrate the smooth transition from ice core to atmospheric measurements. Source: IPCC, 1994a.

dergone intercomparison with ER-2 airplane observations (Tuck *et al.*, 1993), as part of validation exercises. The Cryogenic Limb Array Etalon Spectrometer (CLAES) UARS experiment also measured CH_4 concentrations globally, but results have only been reported so far as sample cases, as additional validation is required prior to releasing this data base (Kumer *et al.*, 1993). Although limited in time and in global coverage, the high spectral-resolution, multiple-species (over two dozen gases) observations made by the shuttle-based Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) instrument during the Spacelab 3 (April-May, 1985), ATLAS 1 (March-April, 1992) and ATLAS 2 (April, 1993) missions (Farmer, 1987; Gunson *et al.*, 1990; Gunson, 1992) are unique “benchmarks” for trends evaluations and for validation exercises.

The paleo record of atmospheric methane concentration has been improved by the analysis of new ice cores (Etheridge *et al.*, 1992; Nakazawa *et al.*, 1993; Blunier *et al.*, 1993; Jouzel *et al.*, 1993; Chappellaz *et al.*, 1993). Antarctic ice core data (Law Dome), which overlap the direct atmospheric measurements, indicate

that the growth rate was not always monotonic, with apparent stabilization periods around the 1920s and again during the 1970s (see Figure 2-7; Etheridge *et al.*, 1992; Dlugokencky *et al.*, 1994a). From Greenland and Antarctic ice cores, Nakazawa *et al.* (1993) conclude that the pre-industrial natural sources in the Northern Hemisphere were larger than those in the Southern Hemisphere. New data from Antarctic Vostok ice core have extended the methane record from 160 thousand year BP (kaBP) through the penultimate glaciation to the end of the previous interglacial, about 220 kaBP (Jouzel *et al.*, 1993). Recent analyses of Greenland ice cores have provided additional climatic and atmospheric composition records (Chappellaz *et al.*, 1993). The methane concentration through the deglaciation is observed to be in phase with temperature. Warm periods, each lasting hundreds of years, are associated with methane peaks of about 100 ppbv. These variations have not been observed in the Antarctic ice cores, likely due to the coarse sampling interval and the slower pore close-off of the Antarctic sites.

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2.4.2 Sources

A detailed discussion of the natural and anthropogenic sources of methane has been given in previous assessments (WMO, 1992; IPCC, 1990, 1992) and only an update is presented here. Methane sources are listed in Table 2-3.

Wetlands. Natural wetlands are the major source of methane and in recent years considerable new data on methane flux from these ecosystems have been published. Recent flux data from the Amazon region suggest that a large fraction of CH₄ is emitted from tropical wetlands (20°N-30°S), with a global estimate of ~60 Tg/yr (Bartlett *et al.*, 1990; Bartlett and Harris, 1993). High northern latitude studies indicate emissions ranging from 20 to 60 Tg/yr (Whalen and Reeburgh, 1992; Reeburgh *et al.*, 1994). Information from large areas of the world is lacking, particularly in the tropics and the Siberian Lowland (Bartlett and Harris, 1993). Recently, atmospheric data have been used to constrain emission estimates from wetlands in the former Soviet Union (Dlugokencky *et al.*, 1994b).

Ocean and Freshwater Ecosystems. A re-evaluation of the ocean source was performed by Lambert and Schmidt (1993). According to these authors only ~3.5 Tg/yr are emitted by the open oceans, but emissions from methane-rich areas could be considerably more important, producing a total oceanic source of the order of 50 Tg/yr. There is no new information about the contribution of freshwater ecosystems.

Termites. A recent estimate made by Martius *et al.* (1993) for the contribution of termites to the global CH₄ budget agrees well with the central value of 20 Tg/yr given in the 1992 IPCC Supplement.

Other Natural Sources. New estimates have been made for volcanoes (3.5 ± 2.7 Tg/yr), hydrothermal emissions (2.3 ± 2.7 Tg/yr), and hydrates (~3 Tg/yr) (Judd *et al.*, 1993; Lacroix, 1993).

Fossil Carbon Related Sources. From studies of the carbon-14 content of atmospheric CH₄ it was established that about 20% (~100 Tg) of total annual CH₄ emission is from fossil carbon sources (IPCC, 1992). However, there are large uncertainties in the contribution of the various related sources: coal mines, natural gas and petroleum industry. New global estimates from coal mines are: 25 Tg/yr (CIAB, 1992), 17 Tg/yr (Müller, 1992), 43 Tg/yr (Beck, 1993), 49 Tg/yr (Subak *et al.*,

1993), and 45.6 Tg/yr (Kirchgessner *et al.*, 1993). Müller (1992) gives an emission from natural gas activities of 65 Tg/yr, which is much higher than the values given in the IPCC (1992) (25-42 Tg/yr). Khalil *et al.* (1993b) proposed that low-temperature combustion of coal (not included previously) could be a significant source of methane, with a global emission of ~16 Tg/yr. However, the emission factor derived by Khalil *et al.* is higher than the values obtained by Fynes *et al.* (1993) from coal-fired plants and the one quoted for handfired coal units by the Air Pollution Engineering Manual (Air and Waste Management Assn., USA, 1992); further research is clearly required to refine this estimate.

Waste Management Systems. Landfills, animal waste, and domestic sewage are significant global sources of methane, with a total emission estimate of ~80 Tg/yr (IPCC, 1992). New global estimates from landfills are 40 Tg/yr (Müller, 1992), 36 Tg/yr (Subak *et al.*, 1993), and 22 Tg/yr (Thorneloe *et al.*, 1993), in good agreement with the mean value (30Tg/yr) given previously (IPCC, 1992). No additional information has been published for animal waste and domestic sewage.

Enteric Fermentation. Anastasi and Simpson (1993) estimated for 1990 an emission of 84 Tg/yr from enteric fermentation in cattle, sheep, and buffalo. This result suggests that the strength of enteric fermentation be in the upper part of the range given in 1992 (65-100 Tg/yr). Furthermore, Minson (1993) in a re-evaluation of this source in Australia found values 43% higher than previous estimates for this country. Johnson *et al.* (1993) estimated a global emission of 79 Tg/yr.

Biomass Burning. New global estimates of this source are: 30.5 Tg/yr (Hao and Ward, 1993), 36 Tg/yr (Subak *et al.*, 1993), and 43 Tg/yr (Andreae and Warnek, 1994). These values are within the range of data reported previously (IPCC, 1992).

Rice Paddies. There is a very large uncertainty associated with the emissions estimate from rice paddies (IPCC, 1992). Three-dimensional (3-D) model calculations constrain estimates of methane emission from rice cultivation to ~100 Tg/yr (Fung *et al.*, 1991; Dlugokencky *et al.*, 1994b). The results reported earlier (IPCC, 1990, 1992) and recent estimates (*i.e.*, Wassman *et al.*, 1993; Delwiche and Cicerone, 1993; Bachelet and Neue, 1993; Subak *et al.*, 1993; Lal *et al.*, 1993; Shearer and Khalil, 1993; Neue and Roger, 1993) suggest an emis-

TABLE 2-3. Estimated sources and sinks of methane (Tg CH₄ per year).

	Range	Likely	Totals
Sources			
Natural			
Wetlands ^a			
Tropics	30-80	~60	
Northern Latitudes	20-60	40	
Others	5-10	10	
Termites	10-50	20	
Ocean	5-50 ^a	10	
Freshwater	1-25	5	
Others ^a	8-13	10	
Total Natural			155
Anthropogenic			
Fossil Fuel Related		100 ^b	
Coal Mines	15-45 ^a		
Natural Gas	25-50 ^a		
Petroleum Industry	5-30		
Coal Combustion	7-30 ^a		
Waste Management System			
Landfills	20-70	30	
Animal Waste	20-30	25	
Domestic Sewage Treatment	?	25	
Enteric Fermentation	65-100	80	
Biomass Burning	20-80	40	
Rice Paddies ^a	20-100	60	
Total Anthropogenic			360
Total Source			515
Sinks			
Reaction with OH ^a	330-560	445	
Removal in Stratosphere ^a	25-55	40	
Removal by Soils	15-45	30	
Atmospheric Increase	30-40	37	
Total Sink			552

^a indicates revised estimates since previous assessments

^b from carbon-14 studies (IPCC, 1992)

SOURCE GASES

sion range of 20-100 Tg/yr with a most likely value of 60 Tg/yr.

2.4.3 Sinks

CH₄ is mainly removed through chemical reactions in the troposphere and stratosphere (485 Tg/yr). A growing number of studies (reviewed by Reeburgh *et al.*, 1994) show that methane is consumed by soil microbial communities in the range between 20 and 60 Tg/yr. Methane oxidation is expected to be particularly important in modulating methane emissions from rice paddies, wetlands, and landfills. Ojima *et al.* (1993) estimate that ~20 Tg of methane is consumed annually by temperate soil, and that this sink has decreased by ~30% due to soil disturbance.

2.4.4 Potential Feedbacks from a Changed Climate

There are several potential climate feedbacks that could affect the atmospheric methane budget (IPCC, 1990). At present, however, the attention has focused on northern wetlands and on permafrost.

High-Latitude Wetlands. Changes in surface temperature and rainfall are predicted by general circulation models (GCMs) to occur in high-latitude regions. When changes in temperature are considered alone, an increase in the emission of CH₄ is predicted (Hameed and Cess, 1983; Lashoff, 1989). Recent calculations suggest only a moderate increase in CH₄ emissions in a 2×CO₂ scenario (Harris and Frolking, 1992). On the other hand, using a hydro-thermal model, Roulet *et al.* (1992) estimated a significant decrease in moisture storage that resulted in an 80% decrease in CH₄ fluxes (negative feedback); the corresponding increase due to temperature changes is only 15%. These estimates have been confirmed by measurements indicating a reduced CH₄ flux from drained northern peatlands (Roulet *et al.*, 1993). It seems that northern wetlands are more sensitive to changes in moisture than temperature; however, the biospheric feedback mechanisms are poorly understood (Reeburgh *et al.*, 1994).

Permafrost. The methane content of permafrost in Fairbanks (Kvenvolden and Lorenson, 1993) and northern Alaska (Rasmussen *et al.*, 1993) was recently evaluated at 2-3 mg/kg. Using these concentrations and the changes in temperature predicted by various

scenarios, Kvenvolden and Lorenson (1993) predict that in 100 years the maximum methane release rate will be ~27 Tg/yr and that during the first 30 years no significant release will occur. The heat transfer and gas diffusion model of Moraes and Khalil (1993) indicates that in the future, permafrost is likely to contribute less than 10 Tg of methane per year.

2.5 NITROUS OXIDE (N₂O)

Nitrous oxide has a long atmospheric lifetime. It is the major source of stratospheric nitrogen oxides, which are important in regulating stratospheric ozone. N₂O is also a greenhouse gas. It is emitted by several small sources, which have large uncertainties, and its atmospheric budget is difficult to reconcile. It is removed by photolysis and oxidation in the stratosphere and microbial oxidation in soils. A reduction of more than 50% of anthropogenic sources would stabilize its concentration at today's level of about 310 ppbv (IPCC, 1994a).

2.5.1 Atmospheric Distribution and Trends

The available global nitrous oxide data indicate that the trend over the past decade is very variable, ranging from 0.5 to 1.2 ppbv/yr (WMO, 1992; Khalil and Rasmussen, 1992). A recent analysis of seventeen years of data collected on oceanic expeditions as well as in Alaska, Hawaii, and Antarctica (Weiss, 1994) and sixteen years of data from the NOAA global network (Swanson *et al.*, 1993) shows that the global average abundance at the beginning of 1976 was 299 ppbv, which has risen to 310 ppbv at the beginning of 1993. During 1976-82 the growth rate was about 0.5-0.6 ppbv/yr, which increased to a maximum of 0.8-1 ppbv/yr in 1988-89, declining to the current rate of 0.5-0.6 ppbv/yr.

An analysis of IR solar absorption spectra recorded at the Jungfraujoch Station (46.6°N) in 1950-51 and from 1984 to 1992 has been recently performed by Zander *et al.* (1994b). The results indicate that the rate of increase of the column of N₂O was 0.23 ± 0.04 for the period 1951 to 1984, and 0.36 ± 0.06 %/yr from 1984 to 1992. The corresponding volume mixing ratios at the levels of the site (3.58 km altitude) increased from 275 ppbv to 305 ppbv between 1951 and 1992. The 1951 concentration is quite similar to the pre-industrial values obtained from ice cores (285 ppbv; IPCC, 1990), sug-

TABLE 2-4. Estimated sources and sinks of N₂O (Tg N per year).

Sources	
A. Natural	
Oceans	1.4-5.2*
Tropical Soils	
Wet forests	2.2-3.7
Dry savannas	0.5-2.0
Temperate Soils	
Forests	0.05-2.0
Grasslands	?
B. Anthropogenic	
Cultivated Soils	1-3
Animal Waste*	0.2-0.5
Biomass Burning	0.2-1.0
Stationary Combustion	0.1-0.3
Mobile Sources*	0.1-0.6
Adipic Acid Production	0.4-0.6
Nitric Acid Production	0.1-0.3
Sinks	
Removal by Soils	?
Photolysis in the Stratosphere*	12.3 (9-17)
Atmospheric increase*	3.1-4.7

* indicates revised estimates since previous assessment

gesting that the pre-industrial level was lower (see below), or that it persisted until the middle of this century and that the increase occurred thereafter.

Satellite global measurements of N₂O have been made by CLAES and ISAMS (Improved Stratospheric and Mesospheric Sounder) aboard UARS (Kumer *et al.*, 1993; Taylor *et al.*, 1993), but no validated results have been released so far.

Ice core records of N₂O show an increase of about 8% over the industrial period (IPCC, 1990). New records covering the last 45 ka were obtained from Antarctica and Greenland (Leuenberger and Siegenthaler, 1992). The Greenland record suggests a pre-industrial level of about 260 ppbv, 10 to 25 ppbv lower than previous records (IPCC, 1990). The Antarctic core shows that N₂O was lower during glacial periods, consistent with

the hypothesis that soils are a major natural source of nitrous oxide.

2.5.2 Sources

A detailed presentation of N₂O sources was made in IPCC (1990) and a revised budget was given in the 1991 ozone assessment (WMO, 1992). N₂O is emitted by a large number of small sources, most of them difficult to evaluate and the estimates are very uncertain. Here we will only present new information not included in previous assessments. The updated budget is presented in Table 2-4. The overall uncertainty in the N₂O budget suggests that it could be balanced with the currently identified sources.

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N₂O fluxes from an upwelling area of the Indian Ocean (Law and Owen, 1990) and the Peruvian upwelling region (Codispoti *et al.*, 1992) indicate that the oceans may be a larger source of this gas. Weiss (1994) calculated that the total pre-industrial source of N₂O was ~9 TgN/yr, of which ~3 TgN/yr was oceanic. An isotopic study (nitrogen-15 and oxygen-18) of atmospheric N₂O suggests a large gross ocean-atmosphere flux (Kim and Craig, 1993). Therefore, the upper range for that source has been extended to 5.2 TgN/yr in this assessment.

Recent emission estimates from some anthropogenic sources made by Subak *et al.* (1993) agree well with previous values. The increasing use of catalytic converters in cars stimulated the evaluation of the global contribution of this source: from tailpipe emission measurements, Dasch (1992) derived a global emission of 0.13 Tg N/yr; Khalil and Rasmussen (1992) from measurements in crowded highways in California estimate a global emission of 0.06-0.6 TgN/yr; Berges *et al.* (1993) from measurements in two tunnels (Stockholm and Hamburg) estimate a global emission of 0.24 ± 0.14 TgN/yr. This new information on N₂O emissions from catalytic converters, together with previous estimates (WMO, 1992) results in a revised emission range of 0.1-0.6 TgN/yr.

Important emissions are produced by agricultural activities. Recent global estimates from fertilized soils are 0.9 TgN/yr (Kreileman and Bouwman, 1994) and 2 TgN/yr (Pepper *et al.*, 1992). A source that was not included in the 1992 Report is cattle and feed lots. Based on the ratios of excess N₂O to excess CH₄ in barn studies, Khalil and Rasmussen (1992) estimate a source of 0.2-0.5 TgN/yr from cattle. Kreileman and Bouwman (1994) estimate for 1990 a global emission of 0.6 TgN/yr for the animal waste source. New information in tropical land use change indicates that the flux of N₂O depends on the age of the pasture, with young pastures (<10 years) emitting 3-10 times more N₂O than tropical forests, whereas older pastures emit less (Keller *et al.*, 1993). A rather low source of 0.2 TgN/yr was estimated by Kreileman and Bouwman (1994) due to enhanced soil N₂O emission following deforestation. More research on tropical agricultural systems is required before conclusions can be reached concerning the relative importance of tropical agricultural systems as a growing N₂O source (Keller and Matson, 1994).

2.5.3 Sinks

The major sink of N₂O is photodissociation in the stratosphere; a secondary loss of about 10% occurs through reaction with O(¹D). The lifetime is 120 ± 30 yr (Prather and Remsberg, 1992). Important evidence of N₂O consumption by soils was reported by Donoso *et al.* (1993), but there are insufficient data to determine whether soil provides a significant global N₂O sink. Based on recent data (Swanson *et al.*, 1993; Weiss, 1994) the atmospheric increase is estimated to be 3.1-4.7 TgN/yr. The estimated sinks (including the atmospheric increase) range from ~12 to ~21 TgN/yr; therefore, to balance the N₂O atmospheric budget, all sources should be near their upper limits. This is in agreement with calculations based on ice core records and atmospheric concentrations that suggest a total anthropogenic emission of ~4.5 TgN/yr and ~9.5 TgN/yr for the natural sources (Khalil and Rasmussen, 1992).

2.6 SHORT-LIVED OZONE PRECURSOR GASES

Tropospheric ozone is a greenhouse gas, of particular importance in the upper troposphere. It also plays a significant role in the oxidizing capacity of the atmosphere. A detailed evaluation of tropospheric ozone is made in Chapter 5. Since the concentration of O₃ depends on the levels of its precursors (*i.e.*, NO_x, CO, CH₄, NMHC), we assess their sources, sinks and atmospheric distributions in the following sub-sections.

2.6.1 Nitrogen Oxides (NO_x = NO + NO₂)

2.6.1.1 TROPOSPHERIC DISTRIBUTION

Because of its complex geographical source pattern and its short lifetime, the spatial and temporal distribution of tropospheric NO_x is complex and highly variable, over 3 orders of magnitude in non urban areas (Carroll and Thompson, 1994). A detailed discussion of the tropospheric distribution of NO_x is presented in Chapter 5.

2.6.1.2 SOURCES

Estimated NO_x source strengths are summarized in Table 2-5.

TABLE 2-5. Estimated sources of NO_x (TgN/yr).

	Range	Likely
Natural Soils	5-12	7
Lightning	3-20	7
Biomass Burning	3-13	8
Subsonic Aircraft	0.2-1	0.4
Fossil Fuel	21-25	24
Agricultural Soils	?	?

Soils. Soil microbial activity is an important natural source of NO_x, but a very large uncertainty affects its estimate (IPCC, 1992). Recently, Williams *et al.* (1992) derived an emission of only ~0.1 TgN/yr from natural soils (grassland, forest, and wetlands) within the U.S. From studies in Venezuela, Sanhueza (1992) estimated an emission of ~4 TgN/yr for the global savannah region. Tropical forest soils produce large amounts of NO; however, due to removal processes inside the forest itself, most of the NO never reaches the "open" atmosphere (Bakwin *et al.*, 1990). Recent global estimates of this source include: Davidson (1991), 13 TgN/yr; Müller (1992), 4.7 TgN/yr; and Dignon *et al.* (1992), 5 TgN/yr.

Agricultural soils could be an important source of NO_x, but no reliable global budgets exist. Cultivated soils from the U.S. emit 0.2 TgN/yr (Williams *et al.*, 1992); plowing of tropical savannah soil produces a large increase of NO emissions (Sanhueza *et al.*, 1994), but the impact to the global budget has not been estimated.

Lightning. The global estimates of NO_x production by lightning show a very large uncertainty (Liaw *et al.*, 1990). Using a global chemistry, transport, and deposition model, Atherton *et al.* (1993) found that a lightning source of 5-10 TgN/yr (with an upper limit of 20 TgN/yr) is compatible with the NO_y levels in remote locations. This is in agreement with Logan (1983), who indicates that the distribution of nitric acid (HNO₃) in the remote troposphere is consistent with a lightning NO_x source of <10 TgN/yr.

Biomass burning. Tropical biomass burning is an important source of NO_x (Crutzen and Andreae, 1990; Lobert *et al.*, 1991; Andreae, 1991; Penner *et al.*, 1991; Müller, 1992), ranging from 2 to 8 TgN/yr. Estimates including extratropical burning indicate global production

of 9.6 TgN/yr (Andreae, 1993) and 13 TgN/yr (Dignon and Penner, 1991).

Aircraft. Emissions from aircraft are a relatively small source of NO. However, since a large fraction of the NO_x is released at altitudes between 9-13 km, this has a large impact on the photochemistry of the free troposphere (Johnson *et al.*, 1992; Beck *et al.*, 1992), and is likely responsible for a large fraction of the NO_x found at those altitudes at northern midlatitudes (Ehhalt *et al.*, 1992). Estimates of the global source from aircraft range from 0.23 to 1.0 TgN/yr (Egli, 1990; Johnson *et al.*, 1992; Beck *et al.*, 1992; Penner *et al.*, 1994). A very detailed evaluation of this source has been recently completed (Baughcum *et al.*, 1993). This study includes emissions from scheduled airliner and cargo, scheduled turboprop, charter, military, and former Soviet Union aircraft. The results indicate a global emission of 0.44 TgN/yr, with 7% of the emission occurring in the Southern Hemisphere. A detailed geographical distribution of this source is given in Chapter 11.

Fossil Fuel Combustion. This is the largest source of NO_x (24 TgN/yr) and its global distribution is relatively well known (Dignon and Hameed, 1989; Hameed and Dignon, 1991; Müller, 1992; Dignon, 1992). According to Hameed and Dignon (1991), the emission of NO_x increased from 18.1 TgN/yr in 1970 to 24.3 TgN/yr in 1986 (25% increase).

2.6.1.3 SINKS

The removal processes of NO_x (atmospheric oxidation of NO_x and dry deposition of NO₂) are reasonably well known. However, it is not possible to make a direct estimate of the global NO_x sink since the global distribution of NO_x is too poorly known.

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TABLE 2-6. Estimated sources of NMHC (TgC/yr).

	Range	Likely
Vegetation*	230-800	500
Oceans	20-150	?
Biomass Burning	30-90	40
Technological	60-100	70

* mainly isoprene and terpenes

2.6.2 Non-Methane Hydrocarbons (NMHCs)

2.6.2.1 ATMOSPHERIC DISTRIBUTION

Most NMHCs (heavier alkanes, alkenes, alkyl benzenes, isoprene, terpenes) have atmospheric lifetimes of less than a week (sometimes less than a day). In this case the atmospheric distributions reflect the source pattern and the regional transport situation, and the mixing ratios generally range from several ppbv in the boundary layer near the sources to a few pptv or less in the background atmosphere. NMHCs with predominantly anthropogenic sources exhibit a maximum in winter, reflecting the seasonality of the removal by OH radicals. Biogenic NMHCs (*i.e.*, isoprene, terpenes) present very low mixing ratios in winter and highest abundance in summer, a consequence of the seasonality of the emission rate (Fehsenfeld *et al.*, 1992).

For NMHCs with lifetimes of few weeks or more (*i.e.*, ethane, acetylene, propane) there is a better understanding of their atmospheric distributions (Ehhalt, 1992; Rudolph *et al.*, 1992). Seasonal cycles and long-term trends in the vertical column abundances of ethane and acetylene above the Jungfraujoch station, Switzerland, have been investigated by Ehhalt *et al.* (1991) and Zander *et al.* (1991b).

2.6.2.2 SOURCES

Estimated source strengths of NMHCs are reported in Table 2-6.

Vegetation. Foliar emissions are, by far, the most important sources of NMHC. Rasmussen (1972) estimated a global emission ranging from 230 to 440 TgC/yr. Zimmerman *et al.* (1978) found that vegetation emits 350 TgC/yr of isoprene and 480 TgC/yr of terpenes. Recently, Müller (1992) reported the following values (in

TgC/yr): isoprene 250, terpenes 147, aromatics 42, and paraffins 52 (total 491 TgC/yr); Allwine *et al.* (1994) estimate a total NMHC emission of 827 Tg/yr.

Oceans. Ehhalt and Rudolph (1984) estimate a global rate from the ocean of 21 TgC/yr (C₂-C₆ hydrocarbons), whereas Bonsang *et al.* (1988) report a much larger rate of 52 TgC/yr. Based on the results of Donahue and Prinn (1990), Müller (1992) indicates that there is a large uncertainty in marine emissions and gives a range of 30-300 TgC/yr.

Biomass burning. Emissions of NMHC from biomass burning range from 36 to 90 TgC/yr (Lobert *et al.* 1991; Müller, 1992; Andreae, 1993). Ethane, ethene, propene, acetylene, and benzene are emitted with a rate >2 TgC/yr (Lobert *et al.*, 1991; Bonsang *et al.*, 1991).

Technological sources. These include gasoline handling, natural gas, refuse disposal, and chemical manufacturing, and produce a global emission ranging between 60 and 140 TgC/yr (Warneck, 1988; Müller, 1992; Piccot *et al.*, 1992; Bouwman, 1993).

2.6.2.3 SINKS

NMHCs react rapidly with the OH radical (unsaturated compounds also react with O₃) and with the exception of ethane (lifetime 2-3 months), their atmospheric lifetimes are shorter than one month; isoprene and terpenes have lifetimes of only a few hours.

2.6.3 Carbon Monoxide (CO)

2.6.3.1 ATMOSPHERIC DISTRIBUTION AND TRENDS

The atmospheric distribution and trends of CO were reviewed previously (WMO, 1992; IPCC, 1992). CO mixing ratios in the troposphere present systematic latitudinal and seasonal variations, ranging from around

TABLE 2-7. Estimated sources and sinks of CO (Tg/yr)

	Range	Likely
Sources		
Technological	300-900	500
Biomass Burning	400-700	600
Biogenics	60-160	100
Oceans	20-190	?
Methane Oxidation	400-1000	600
NMHC Oxidation	300-1300	600
Sinks		
OH Reaction	1400-2600	2100
Soil Uptake	250-640	250
Stratospheric Remotion	~100	100

40 to 200 ppbv. Annual mean CO levels in the high latitudes of the Northern Hemisphere are about a factor of 3 greater than those at similar latitudes in the Southern Hemisphere.

During the 1980s there was evidence that atmospheric CO was increasing at ~1%/year in the Northern Hemisphere, whereas no significant trend was observed in the Southern Hemisphere (WMO, 1992). Recent measurements indicate that global CO levels have fallen sharply from the late 1980s. Novelli *et al.* (1994) found that in the Northern Hemisphere, CO decreased at a spatially and temporally average rate of 7.3 ± 0.9 ppbv/yr (6.1 %/yr) (June 1990 to June 1993), whereas in the Southern Hemisphere it decreased at 4.2 ± 0.5 ppbv/yr (7.0 %/yr). Khalil and Rasmussen (1994) for the period 1987 to 1992 reported a decrease of 1.4 ± 0.9 %/yr in the Northern Hemisphere and 5.2 ± 0.7 %/yr in the Southern Hemisphere. While the above results concern surface levels of CO, total vertical column abundances of CO above the Jungfrauoch station, Switzerland, also show a mean rate of decrease equal to 1.15 ± 0.32 %/yr between 1985 and 1993 (Zander *et al.*, 1994c). The causes of this behavior have not been identified, but decreases in tropical biomass burning and Northern Hemisphere urban emissions have been suggested. The total amount of CO in today's atmosphere is less than it was a decade ago.

Preliminary global and seasonal variations of CO between 30 and 90 km altitude have been reported by

Lopez-Valverde *et al.* (1993), based on ISAMS/UARS infrared limb emission measurements. These are the first global measurements of CO in the middle atmosphere, with data validation being still in progress.

2.6.3.2 SOURCES

Estimated strengths of sources and sinks of CO are summarized in Table 2-7.

Technological sources. Technological sources include transportation, combustion, industrial processes, and refuse incineration. There are several evaluations (Jaffe, 1973; Logan, 1980; Seiler and Conrad, 1987; Cullis and Hirshler, 1989; Khalil and Rasmussen, 1990; Müller, 1992; Subak, *et al.*, 1993) ranging from 300 to 900 TgCO/yr.

Biomass burning. Recent estimates for the tropics range from 400-700 TgCO/yr (Lobert *et al.*, 1991; Müller, 1992; Andreae, 1993; Subak *et al.*, 1993). Including extratropical burning, Andreae (1993) derives a global source equal to 621 TgCO/yr.

Terrestrial biogenic sources. These include vegetation, soils, and animals (*i.e.*, termites). Based on the emission rates found on higher plants of the temperate region, Seiler and Conrad (1987) estimated a global source of 75 ± 15 TgCO/yr. Assuming CO emissions proportional to net primary productivity (NPP) and using the flux reported by Kirchoff and Marinho (1990) for tropical forests, Müller (1992) evaluated a global

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biogenic source at 165 TgCO/yr. Photoproduction of CO from dead plant matter has been reported (Valentine and Zepp, 1993; Tarr *et al.*, 1994), however, no global evaluation of this source has been made.

Oceans. Early estimates of CO emissions from the oceans (IPCC, 1992) range from 20 to 190 TgCO/yr. Using an atmospheric general circulation model, Erickson (1989) calculated a global ocean source equal to 165 ± 80 TgCO/yr.

Hydrocarbon oxidation. This is the most important source of atmospheric CO. The production of CO from methane oxidation ranges from 400 to 1000 TgCO/yr, and 300 to 1300 TgCO/yr from NMHC (Zimmerman *et al.*, 1978; Logan, 1980; Khalil and Rasmussen, 1990; Crutzen and Zimmerman, 1991).

2.6.3.3 SINKS

Reaction with the OH radical is the major sink for CO. Soil uptake and removal in the stratosphere are minor sinks. In principle, the atmospheric removal rates for CO can be calculated from the atmospheric CO distribution, the distribution of the OH radical concentration, and the related reaction rate. Model calculations predict a removal rate of about 2000 Tg(CO)/yr (WMO, 1986; Seiler and Conrad, 1987; Khalil and Rasmussen 1990; Crutzen and Zimmerman, 1991).

2.7 CARBON DIOXIDE (CO₂)

The change in atmospheric concentration of CO₂, from 280 ppmv pre-industrial to ~360 ppmv in 1993, is the major contributor to the calculated increase in radiative forcing since the pre-industrial period (*i.e.*, 1.5 W m⁻²). An updated review of the CO₂ budget has been made in the 1994 IPCC report (IPCC, 1994b).

Observations of CO₂ since the 1950s show systematic upward trends, in both concentration and rate of concentration increase, albeit with substantial variation in the rate of increase from year to year. During the period 1991 to 1993, the rate of increase of CO₂ per year slowed substantially (to as low as 0.5 ppmv/yr from the long-term average of 1.5 ppmv/yr). There are numerous examples in the record of short periods where growth rates are higher or lower than the long-term mean. The most recent observations indicate that growth rates are now increasing again (IPCC, 1994b).

CO₂ emission from industrial processes (mainly fossil fuel combustion and cement production) in 1991 is estimated at 6.2 GtC/yr (Andres *et al.*, 1994), compared with 6.0 ± 0.5 GtC in 1990 (IPCC, 1992). The cumulative input since the pre-industrial period is estimated at 230 GtC (Andres *et al.*, 1994). Recent satellite remote sensing measurements of land clearing rates in the Brazilian Amazon have resulted in substantially reduced estimates (by ~50%) for this area (INPE, 1992; Skole and Tucker, 1993). However, deforestation rates for the rest of the tropics remain poorly quantified. Current net flux estimates (in GtC/yr) that include regrowth after deforestation are: 0.6 for Latin America, 0.7 for South and Southeast Asia, 0.3 for Africa, and -0.3 to -1.1 for mid/high latitudes, producing a global mean for the 1980s of 1.1 ± 1.2 GtC/yr (IPCC, 1994b). The oceans represent a significant sink of atmospheric CO₂, averaging 2.0 ± 0.8 GtC/yr over the decade 1980-89.

The imbalance between atmospheric concentration changes, estimated emissions, and estimated ocean uptake, as well as the discrepancies between the observed and calculated inter-hemispheric gradients of CO₂, indicate the existence of an unaccounted-for terrestrial sink of 1.2 ± 1.6 GtC/yr, probably attributable to a combination of CO₂-induced plant growth (0.5-2.0 Gt/yr), nitrogen fertilization (0.2-1.0 Gt/yr), and possible climatic effects (0-1.0 Gt/yr) (IPCC, 1994b).

Climatic feedback appears to be positive, amplifying the effect of anthropogenic emissions, although this amplification may be reduced due to feedbacks and compensating processes within the marine and terrestrial systems. It is likely that the effect of CO₂ fertilization on plant production will be substantially smaller than the 20-40% observed in most agricultural plants. An important body of data supports the view that responses of plant production to elevated CO₂ are restricted in nutrient-limited ecosystems (*e.g.*, Díaz *et al.*, 1993); however, it is possible that N deposition arising from the use of fertilizers and fossil fuel combustion will reduce the intensity or spatial distribution of nitrogen limitation.

Carbon cycle modeling studies of CO₂ concentrations, under a range of emissions scenarios and for a range of stabilized CO₂ concentrations up to 750 ppmv, yield the following results (IPCC, 1994b): i) because of the long residence time for carbon dioxide, stabilization of anthropogenic emissions at projected 2000 levels (from IS92a scenario) leads to a nearly constant rate of

increase in atmospheric concentrations for at least two centuries; modeled concentrations reach 480-540 ppbv by 2100; ii) stable CO₂ concentration at values up to 750 ppmv can be maintained only with anthropogenic emissions that eventually drop below 1990 levels; iii) there is a close relationship between the eventual stabilized concentration and the integrated CO₂ emission from now until the time of stabilization. Integrated emissions for stabilization at levels lower than 750 ppmv are less than those calculated for the IS92 a, b, e, and f scenarios.

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